RADIATION-INDUCED PROCESSING OF HYDROCARBONS IN ENVIRONMENTS RELEVANT TO PLUTO

by

Midshipman Robert M. Gallagher, Class of 2001
United States Naval Academy
Annapolis, Maryland

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Certification of Advisor Approval

Professor Robert F. Ferrante
Chemistry Department

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Acceptance for the Trident Scholar Committee

Professor Joyce E. Shade
Chair, Trident Scholar Committee

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Spectroscopic observations of Pluto suggest the presence of ethane, presumably caused by cosmic ray irradiation of methane trapped in solid nitrogen at the surface. This project used near-infrared (NIR) spectroscopy to examine this process in laboratory analogs. Samples of nitrogen doped to appropriate low concentrations with methane and/or carbon monoxide were deposited at 50 K or below, and the resulting films irradiated with varied doses of 1 MeV protons. The formation of ethane, and other products, was observed at radiation dosages consistent with levels experienced at the planet's surface. However, neither the intensity nor bandwidths of the spectroscopic signals compared very well with the NIR telescope data. These facts lend some support to a model suggesting two different terrains on the planet, one with low methane concentration, and another with much higher levels. Irradiation of the latter might account for ethane signals observable from earth. The laboratory irradiation experiments also resulted in the formation of a residue, stable at high temperatures, consistent with models of organic polymer formation on icy bodies in the outer solar system. Some attempts at determining the composition of the residue were also performed.

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I. <u>Introduction</u>

It is widely accepted that approximately four and a half billion years ago, the planets of our solar system formed from a thin, extended disk of matter that orbited the Sun (see Figure 1). Some of this matter formed the planets, and some weakly bonded material escaped the system altogether. The remaining matter in the protoplanetary disk formed the planetesimals, comets, and asteroids. The general compositions of these space objects varied as the distance from the sun increased. The rocky planets and the asteroids formed from refractory material closer to the Sun. It is believed that comets and other objects of the outer solar system formed in the colder, more distant regions of the protoplanetary disk, where the more volatile components condensed as ices. A distinct group of these objects of the outer solar system is classified as the Edgeworth-Kuiper Belt. The belt is defined as a disk-shaped region containing icy planetary bodies lying mostly within the plane of the planets, beyond the orbit of Neptune, or more than 30 AU (astronomical units) from the Sun. These icy bodies are termed Edgeworth-Kuiper Objects (EKOs).
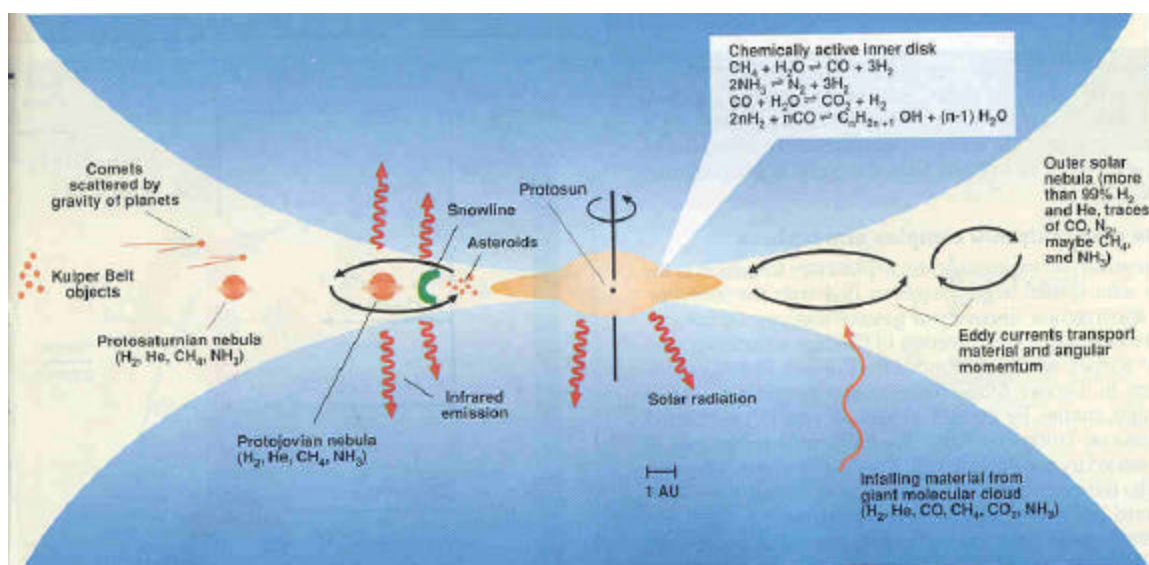
Figure 1: Theory describing the origin of the solar system by a chemically active protoplanetary disk (Lunine 1995)

Some comets are generally accepted to represent a population of small EKOs injected into the inner solar system, mainly by planetary perturbations. Centaur objects, such as Chiron and Pholus, are considered to be in a transient phase from EKOs to short period comets (Nakamura et al. 2000). Recent near-infrared spectroscopy has revealed diverse surface compositions among Centaur objects (Luu et al. 1994) and EKOs (Luu, Jewitt 1998; Brown et al. 1997). The variations in surface composition reflect the effect that orbital size (distance from the Sun) has had on the alteration process in the protoplanetary disk, which is characterized by cosmic ray irradiation and thermal processing.

Recently, Pluto and Triton have been considered to be the largest members of the EKOs. Questions have even been raised concerning the accuracy of Pluto's classification as a planet. The near-infrared spectra of Pluto and Triton show absorption features of solid methane and carbon monoxide diluted by nitrogen ice (Owen et al. 1993; Quirico et al. 1999). Pluto also has a large satellite, Charon, which has near-infrared features

showing mostly water ice, although Pluto and Charon could not be spatially resolved by ground-based telescopes until very recently.

Pluto still remains the only planet in our solar system that is yet to be observed by a close spacecraft flyby. This being the case, improvements in ground-based spectrophotometry have dramatically increased our capabilities to determine surface properties. The Subaru telescope with CISCO (Cooling Infrared Spectrograph and Camera for OHS (OH-airglow suppressor)) uses the latest technology for ground-based astronomical observations of the outer solar system (Nakamura et al. 2000). The Subaru telescope is one of the first ever to spatially resolve Pluto from Charon and record independent near-infrared spectra of each. These improved observational capabilities allow for a much more detailed analysis of the icy worlds of the Edgeworth-Kuiper Belt.

Due to their great distances from the sun, EKOs are believed to provide the best historical record of objects formed at the edge of our solar system. The purpose of this project is to present experimental findings concerning the viability of cosmic ray irradiation as the mechanism by which organic molecular processing occurs on the surface of Pluto. The project provides theoretical support for ground-based observational data and also reports some predictions of chemicals on Pluto that may only be present in trace amounts. These species, presumably products of comic ray processing, are not yet detectable from the ground, but may be detected by spacecraft flybys with high resolution spectrometry in the future. Radiation products of EKO ices may also have some exobiological significance. Many solar system ices, rich in nitrogenous and carbonaceous molecules, have been known to form hazy organic residues known as "tholins" when irradiated (Khare et al. 1984). It is suspected that these tholins, when

introduced into an 'energetic' (characterized by high levels of electrical and geothermal activity) liquid water environment, are capable of generating significant prebiotic molecules like amino acids. Indeed, the radiation chemistry of EKOs is a significant scientific endeavor that may have important implications concerning the evolution of our solar system and the origin of life on Earth.

II. Background and Theory

A. Infrared Spectroscopy

Molecules are not static entities. They are oscillating bundles of atoms held together by the energy in their chemical bonds. Infrared spectroscopy allows one to observe the vibrations of molecules and provides evidence of the atom combinations and chemical bonds present. This process begins when a sample is irradiated with electromagnetic waves or photons, over a range of energies, in order to excite vibrational modes in the molecules present within the sample. This electromagnetic radiation is non-ionizing radiation (unlike proton irradiation), and therefore, infrared spectroscopy is a non-destructive form of chemical analysis. A photon of frequency ν (or wavelength λ) has an energy given by

$$\varepsilon = h\nu = (hc)/\lambda \qquad (1)$$

where c is the speed of light and h is Planck's constant. During spectroscopy, some of the photons will excite vibrations, of characteristic frequencies, in specific chemical bonds within the sample. The characteristic vibrating frequency for a given bond is dependent on the mass of the atoms in the bond and the bond energy.

A covalent chemical bond between two atoms acts like a spring (see Figure 2). When the bond is stretched, a restoring force pulls the two atoms together, toward their equilibrium bond length. If the bond is compressed, the restoring force pushes the two atoms apart. If the bond is stretched or compressed and is then released, the atoms vibrate. The frequency of this vibration decreases with increasing atomic weight of the bonded atoms and increases with bond energy (Wade 1999).

A stretching vibration
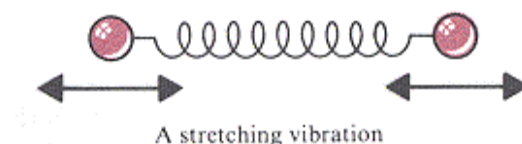
Figure 2: Comparison of the stretching vibration of a covalent bond to the motion of an oscillating spring

Along with stretching vibrations, molecules also undergo bending vibrations when absorbing specific energies of electromagnetic radiation. In a bending vibration, the bond lengths stay constant, but the bond angles vibrate about their equilibrium values.

Figure 3: The effects of stretching and bending vibrations on the infrared spectrum of an organic molecule

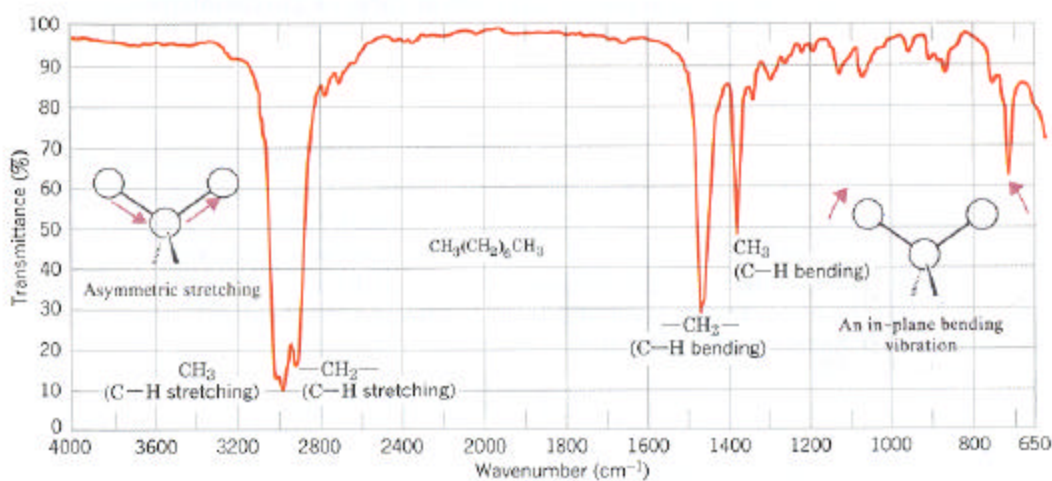An infrared spectrometer measures the frequencies (or energies) of infrared light absorbed by a compound as it experiences its different vibrational modes. After the infrared beam of a spectrometer passes through a sample, the beam enters a detector that measures the intensity of infrared light transmitted through the sample as a function of frequency. The frequencies of light that are not transmitted with great intensity have been absorbed by the sample (see Figure 3). The transmission data is referenced to the intensity of the original infrared beam, generating an absorption spectrum that illustrates the intensity of absorption as a function of wavelength. This is referred to as the infrared absorbance spectrum of the sample. Figure 4 shows a schematic of a Fourier transform infrared spectrometer, similar to the one used in this project.
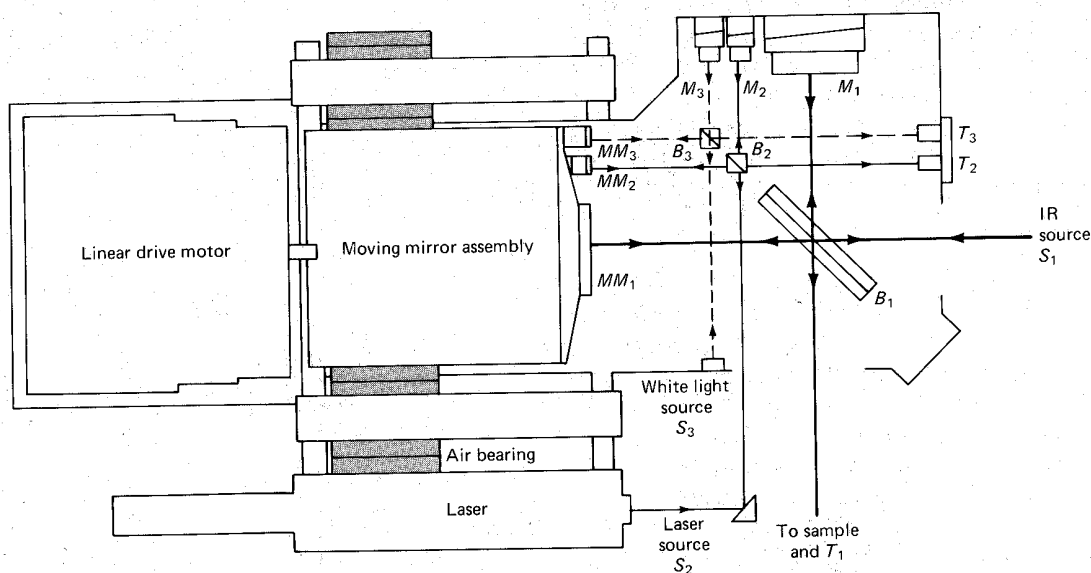

Figure 4: Schematic of a Fourier Transform Infrared Spectrometer

This experiment specifically utilized near-infrared (NIR) spectroscopy, which means that sample absorbance was measured over wavelengths from 2.50 microns to 1.25

microns (or wavenumbers from 4000 to 8000 cm^{-1}). The near-infrared is the region of choice for spectroscopy relevant to space objects and is consistent with observational data of Pluto. Mid-infrared (MIR) spectroscopy was also utilized in the laboratory because most of the ice analogs studied in this project have their strongest absorbance features in the MIR. Use of the MIR region involved spectroscopy from wavelengths of 12.5 microns to 2.5 microns (or wavenumbers from 800 to 4000 cm^{-1}).

B. Gas Chromatography – Mass Spectrometry (GC-MS)

Gas chromatography – mass spectrometry (GC-MS) is a process in which a sample mixture is separated into its various constituents, each constituent is ionized, and the ions are sorted by mass, providing structural and compositional information regarding the molecules present in the sample. Gas chromatography (GC) separates the sample mixture into its components by passing it through a metal column, packed with substrate material, to which the molecules adsorb to varied extents. The temperature of the column is increased, and each purified constituent of the sample is detected as it evaporates from the column. The time at which each constituent exits the column depends on the temperature of the column, the affinity of the sample molecules for the substrate material, the volatility of the sample, and the affinity of the molecules of each constituent for molecules of other constituents of the sample. Upon exiting the GC column, each purified constituent is passed into the intake of the mass spectrometer (MS).

Mass spectrometers first ionize and fragment the molecules of the sample by passing them through an electron beam, inducing electron impact ionization and molecular fragmentation. The fragmented ions are then separated by magnetic

deflection. The positively charged ions are attracted to a negatively charged acceleration plate, and the ion beam is steered through an evacuated flight tube. The flight tube contains a curved portion positioned between the poles of a large magnet (see Figure 5). When charged particles pass through the magnetic field, a transverse force bends their path (Wade 1999). The path of heavier ions bends less than the path of lighter ions, and by this relationship, ions are sorted by mass, using a detector to measure the alteration of the ion path.
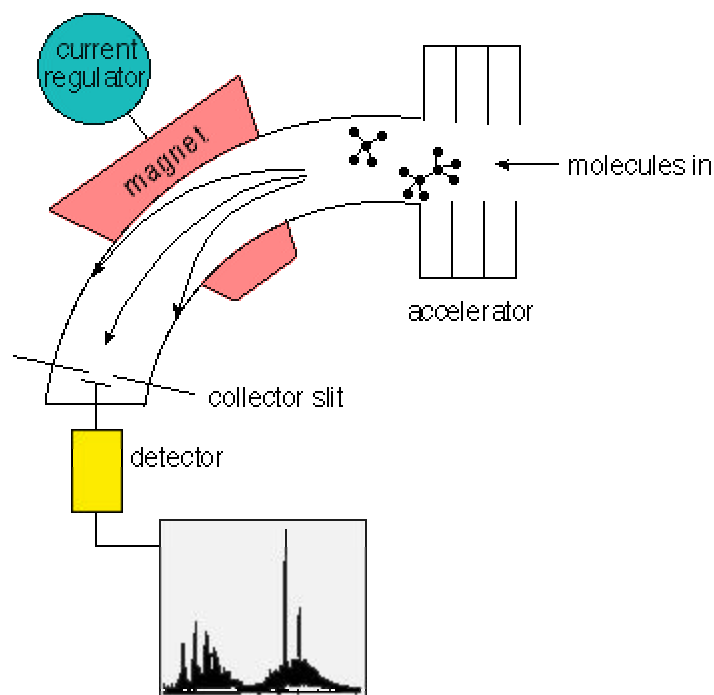

Figure 5: Schematic diagram of a magnetic deflection mass spectrometer

The actual mass spectrometer that is integrated into the GC-MS instrument is a quadrupole mass spectrometer, which is slightly different than the magnetic deflection type. The mass-sensitive detector in the GC-MS instrument is a quadrupole type, where

alternating electrical fields replace the magnet as a mass filter, and only allow ions of specific mass to reach the detector.

Mass spectra are often useful in determining the molecular weight of the sample molecules. Structural characteristics are also commonly apparent based on the characteristic fragmentation patterns described by mass spectra. For these reasons, GC-MS is a useful tool for analyzing unpurified samples of unknown composition. GC-MS was used in this project to analyze the organic residues generated by proton irradiation and thermal processing of cosmic ice analogs.

C. The Space Environment

This project used laboratory procedures to simulate the effects of the space environment on EKOs - a process known as 'space weathering.' The primary form of space weathering is the radiation to which the EKOs are exposed. Of the multiple natural sources of radiation in space, galactic cosmic rays (GCRs) comprise the most significant radiation source to the Plutonian and Edgeworth-Kuiper Belt environment. GCRs are energetic nuclei originating outside the solar system, produced either by nova or supernova explosions in other star systems or accelerated by the interstellar fields. Galactic cosmic radiation consists of a flux of energetic, $10^8 - 10^9$ eV, ionized nuclei (~85% protons) that appear to fill our galaxy isotropically (Tribble 1995). Pluto receives more energy in the upper several meters of its surface from GCRs than from the Sun's ultraviolet radiation, which is only deposited in the upper few millimeters of the surface (Johnson 1989). High energy protons in GCRs impart an energy dose of 2.6 x 10^{18} eV/cm^2 on the Plutonian surface every orbit (Johnson 1989).

Space is also a vacuum environment, with very low temperatures on the icy EKOs, at their distant range from the sun. Based on recent observations, the surface temperature of Pluto has been estimated as low as 40 K (-388°F) (Tryka et al. 1994). These features of the space environment shaped the experimental conditions applied to samples in this project. Laboratory experiments were designed to simulate a high flux of energetic protons on cosmic ice analogs in a vacuum environment, at temperatures as low as 30 K (-405° F). Although the experimental design of this project only allowed for 10^6 eV (1 MeV) proton irradiation and pressures as low as 10^{-7} torr, it provided a reasonable simulation of the space environment – nearly the best that could be expected for Earth-based experimentation.

D. Past Plutonian Observations

Pluto and Charon have been found to constitute a binary planet system in which Pluto, with a diameter of 1164 $\pm$ 22.9 km, has almost exactly twice the diameter of Charon at 621 $\pm$ 20.6 km (Young and Binzel 1994). The Pluto-Charon Binary (PCB) travels in a highly eccentric (elliptical) heliocentric orbit with a perihelion (closest point of approach to the sun) of 29.67 AU and an aphelion (peak orbital distance from the sun) of 49.95 AU.

Methane ice was discovered on Pluto in 1976 (Cruikshank et al. 1976), before the existence of the satellite, Charon, was known. Owen et al. (1993) discovered nitrogen (N_2) and carbon monoxide (CO) in the spectrum of Pluto through an advance in

spectroscopic instrumentation for ground-based observation. After the discovery of Charon in 1977, differentiated spectra of the two bodies were achieved during periods of eclipse between Pluto and Charon in the mid-1980s (Cruikshank et al. 1998). Again, technological advances have increased the capabilities for ground-based observations, and the Subaru telescope has very recently collected data of Pluto and Charon that boast some of the best spectral and spatial resolution ever achieved by ground-based spectroscopy of the PCB. The basic surface composition of Pluto is presently reported to exist as a solid ice mixture of N_2, CH_4, and CO in a 1:0.01:0.002 ratio, respectively (Nakamura et al. 2000). However, recent models suggest regions of pure methane or regions of highly concentrated methane in solid nitrogen ice as well as the presence of a solid crust of complex organics (Doute et al. 1999).

E. Subaru Telescope Spectroscopic Observation

The National Astronomical Observatory of Japan (NAOJ) operates the Subaru optical-infrared telescope at the summit of Mauna Kea, Hawaii. Astronomers using the telescope observed the PCB from 1400 UT (universal time is equivalent to Greenwich mean time) until 1447 UT on 6 May 1999 and from 1228 UT until 1251 UT on 10 June 1999 using CISCO mounted on the Subaru telescope (Nakamura et al. 2000). The observation was taken in the NIR region at wavelengths from 2.0 – 2.5 microns. Observations of Charon were clearly separated from Pluto on both observation dates. The high quality observational data (see Figure 6) provided by the Subaru telescope has facilitated more detailed laboratory investigations of Pluto and other EKOs, than had

been possible in the past. The availability of such precise data from the very ends of our solar system has allowed laboratory endeavors to finally examine some of the natural processes that occur at the icy worlds of the outer solar system.
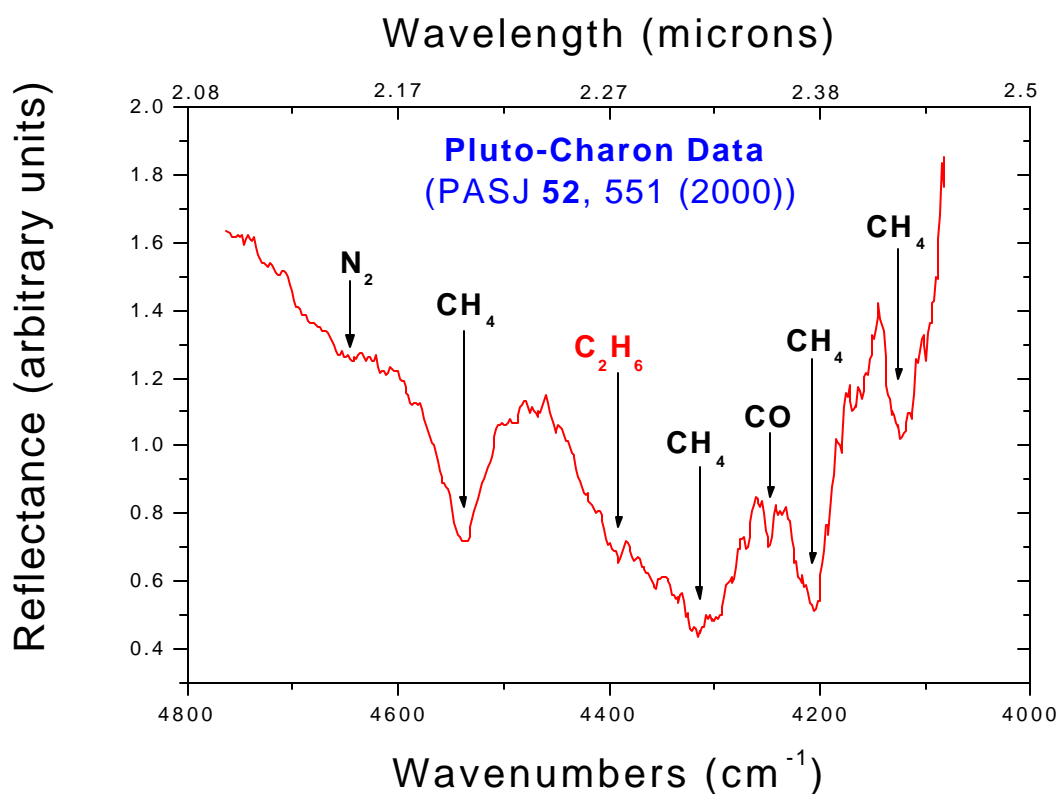

Figure 6: An observational spectrum of the Pluto-Charon system, recorded using the Subaru telescope

III. **Experimental Design**

The goal of this project was to simulate the 'space weathering' that occurs on the icy surfaces of EKOs like Pluto. This was accomplished in the Cosmic Ice Laboratory of Dr. Marla Moore of the Astrochemistry Branch at NASA Goddard Space Flight Center in Greenbelt, Maryland.

The keys to performing a laboratory simulation of space weathering are (1) achieving a low temperature (30 K or -405° F) test area and maintaining the ability to slowly adjust the temperature of the system, (2) maintaining a high vacuum through the use of an air-tight apparatus and pumping systems, (3) having a mechanism for the deposition of volatile chemical species onto the cold test area, (4) irradiating the sample with high energy protons or ultraviolet rays (ionizing radiation), and (5) having the ability to monitor sample composition and the formation of new species.

A. Formation of Simulated Solar System Ices

Simulated solar system ices were deposited onto a silicon substrate, housed within the sample chamber of a closed cycle helium cryostat. The cryostat system achieved temperatures as low as 30 K within the sample chamber and it was connected to a vacuum system that provided low pressure ($\sim 10^{-7}$ torr) within the test chamber (see Figure 7). A glass bulb containing the gaseous mixture of the desired chemical species was attached to a gas handling system (see Figure 8). This mixture was then allowed to flow through a regulator valve leading to a capillary tube, through which the mixture entered the sample chamber and deposited onto the silicon substrate. Typically, ices were deposited to a thickness ranging from 10 ìm to 20 ìm. Ice thickness was determined by the frequency at which repeated film interference fringe peaks occurred in the infrared spectrum of the ice, as it was being deposited. The thickness, t, of the ice (in ìm) was calculated using the equation:

$$t = \frac{1}{2(\Delta \boldsymbol{n})} * \frac{10^4}{n} \qquad (2)$$

where Äv is the separation (in cm^{-1}) of two sequential film fringe peaks, the factor or 10^4 accounts for the conversion from cm to ìm, and n is the index of refraction of the ice material (for N$_2$, n=1.26).
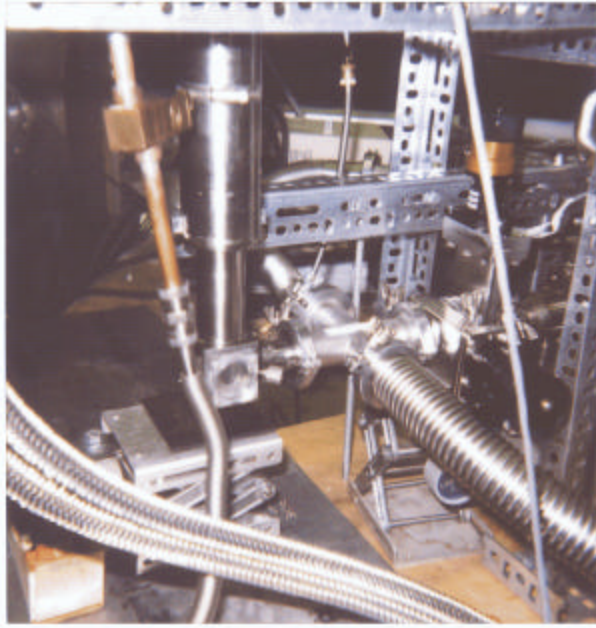

Figure 7: Photograph of the cryostat or 'cold finger' (the vertically oriented silver cylinder). The gas deposition tube can be seen running into the sample chamber at the base of the cold finger. Other tubes running through the picture are part of the pumping systems that minimize the pressure in the test chamber.
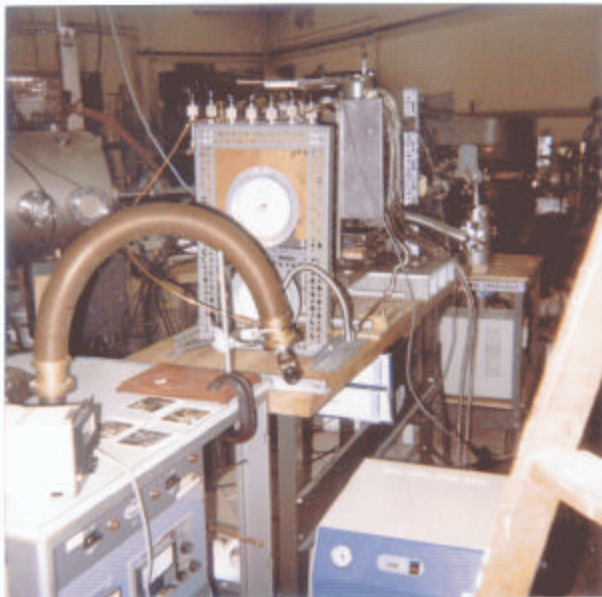

Figure 8: Photograph of the gas handling system (the rectangular structure with the round, white pressure gauges and black valves on top). This system allows the experimenter to load a gas mixture and slowly deposit it into the cold sample chamber. The amount of deposition is determined by the pressure change in this system.

B. Identification of Ice Samples

The sample chamber containing the ice on its silicon substrate was oriented within the optical beam of a Bruker Fourier Transform Near-Infrared (FT-NIR) spectrometer. This instrument generated the absorbance spectrum of the ice over a broad range of infrared wavelengths (25 microns to 1 micron). The sample chamber, equipped with infrared transmitting salt windows on opposite sides of the ice sample, allowed the infrared beam to pass through the sample and the windows for transmission spectroscopy (see Figures 9 and 10). Using the spectrum, the chemical species present in the ice were identified, based on the wavelengths at which they absorbed. The spectrometer and the entire vacuum system were located within a high radiation facility and the spectrometer was, therefore, operated remotely from a computer in an adjacent laboratory. This remote operation allowed for simultaneous spectroscopy and irradiation of the sample.
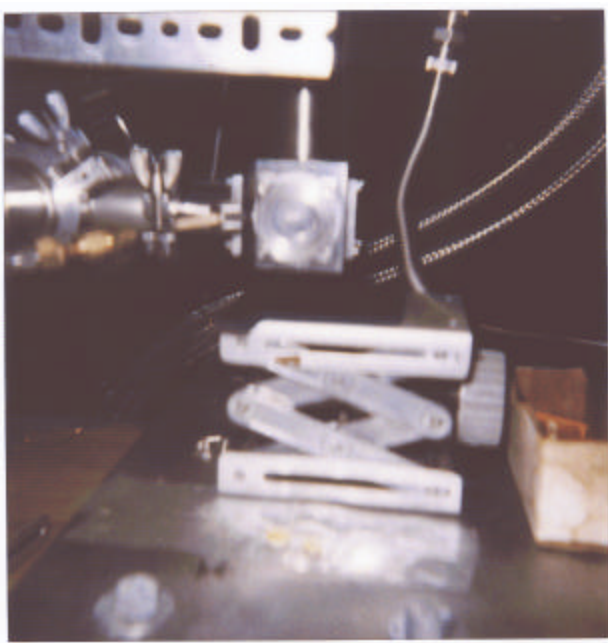

Figure 9: Photograph of the sample chamber showing one of its salt windows, through which the optical beam of the spectrometer passes. The proton beam from the Van de Graaff accelerator enters the sample chamber from the left side of this picture. The sample is oriented at a 45° angle to both of these beam lines.

C. Irradiation of Ice Samples

Cosmic rays incident on Pluto and other EKOs were simulated in the laboratory using a Van de Graaff particle accelerator capable of accelerating protons to energies as high as 1.5 million electron volts (MeV). The Van de Graaff accelerator (see Figure 11) was rigidly attached to the sample chamber, allowing the proton beam line to directly intersect the sample area on the silicon substrate. The substrate was oriented at a 45° angle to both the infrared beam of the spectrometer and the proton beam from the accelerator (which ran perpendicular to each other), as seen if Figure 10. This allowed for simultaneous irradiation and spectroscopy without the need for moving the ice sample.
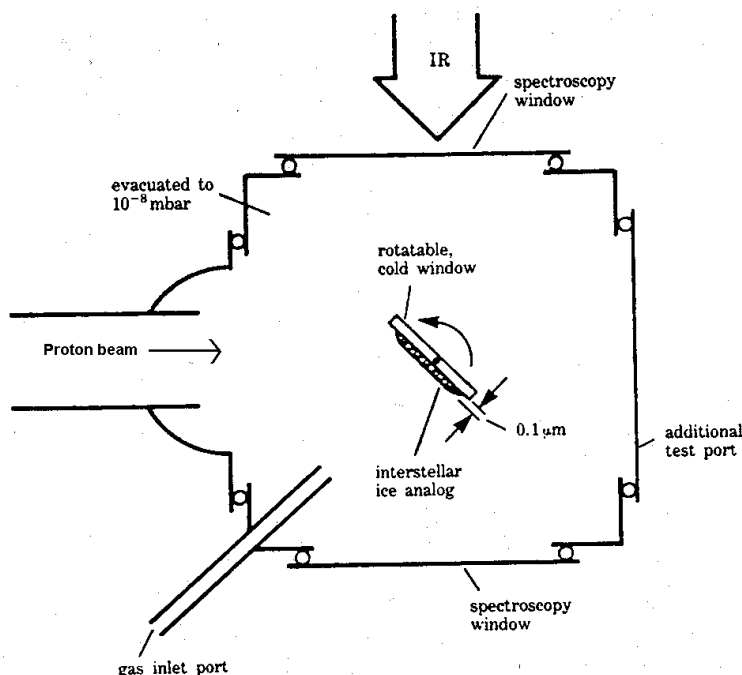
Figure 10: Schematic of the test chamber. The proton beam from the Van de Graaff accelerator and the optical beam of the spectrometer run perpendicular to each other so that both may align with the sample ice simultaneously.

High-energy protons that impact the cosmic ice analog break chemical bonds, forming molecular fragments within the ice matrix. These molecular fragments are radiation products, and they also act as the starting material from which other radiation products form. When the newly formed molecular fragments diffuse through the sample ice and recombine, larger molecules (different from the starting material) can be formed. Diffusion is hindered at low temperatures, so most diffusion occurs during thermal processing, and it is at this time that larger molecules can be expected to form from other radiation products. Spectroscopy was performed at intermediate radiation dosages to determine the chemical identity of any radiation products and to qualitatively evaluate their rate of production with respect to the radiation dosage.

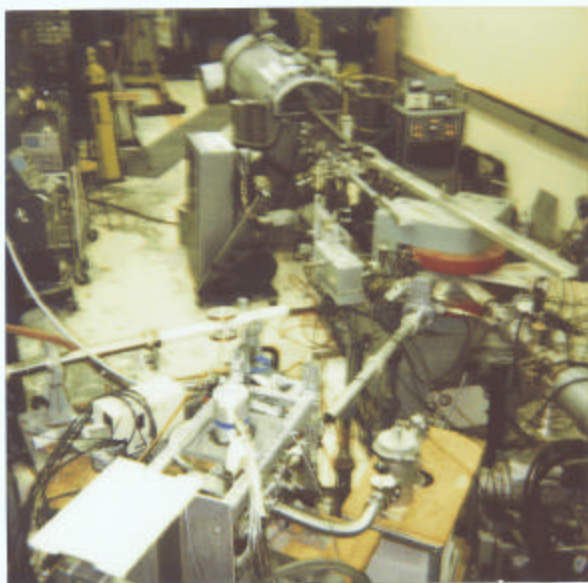Figure 11: Photograph of the Van de Graaff particle accelerator (the large cylinder in the upper portion of the picture). The accelerator ionizes hydrogen gas to produce protons and accelerates these charged particles through its beam line. An electromagnet (red ring at right center) is used to steer the proton beam into the desired tube within the accelerator room. The cryostat used in this study appears at the lower left.

D. Thermal Processing

As Pluto travels through its orbit around the sun, it experiences some thermal variations due to varying solar flux, and the high eccentricity (elliptical shape) of its orbit. As a result of these thermal variations at Pluto, surface temperatures may vary between 35 K and 55 K. To account for this process in laboratory ice analogs, a heater was incorporated into the cryostat system, allowing for a slow warm-up of the sample. By stopping the warm-up process at various increments and recording infrared spectra of the sample, the effects of the thermal processing on the irradiated sample could be discovered.

In general, it was expected that new products would be detected during the warm-up process because the warmer temperature allows some of the molecular fragments, which resulted from irradiation, to move freely about the ice matrix and recombine. Likewise, thermal processing results determine the impact which orbital variation has on surface properties.

IV. **Results and Discussion**

A. Modeling the Plutonian Surface Composition

Analysis to construct a model of Pluto's surface composition was undertaken using two general methods. One method consisted of correlating infrared spectra of laboratory ice mixtures with observational spectra provided by astronomers. The other method involved using laboratory radiation experiments to determine radiation products expected on the Plutonian surface, based on the radiation environment of the planet.

1. Effect of Temperature on Infrared Peak Positions

Ice temperature has been shown to affect the infrared peak positions of CH_4 in N_2 ices (see Figure 12). These effects exist because of a phase change in N_2 ice from á-N_2 to â-N_2 at 35.6K, and because CH_4 infrared peaks are shifted toward shorter wavelengths relative to pure CH_4 as the temperature decreases below ~40K (Cruikshank et al. 1998). These temperature related effects on infrared peak positions in the observational spectra of Pluto, can essentially be used as a 'thermometer' to determine the temperature of the planet's surface ice (Doute et al. 1999). Using this method to analyze the observational spectrum of Pluto, Tryka et al. (1994) determined that Pluto contained â-N_2 with an average temperature of approximately 40K, at the times when observational spectra were recorded in recent years. For this reason, all of the ices presented in this paper are ices of â-N_2, and all ice mixtures were irradiated at approximately 35K – 40K.
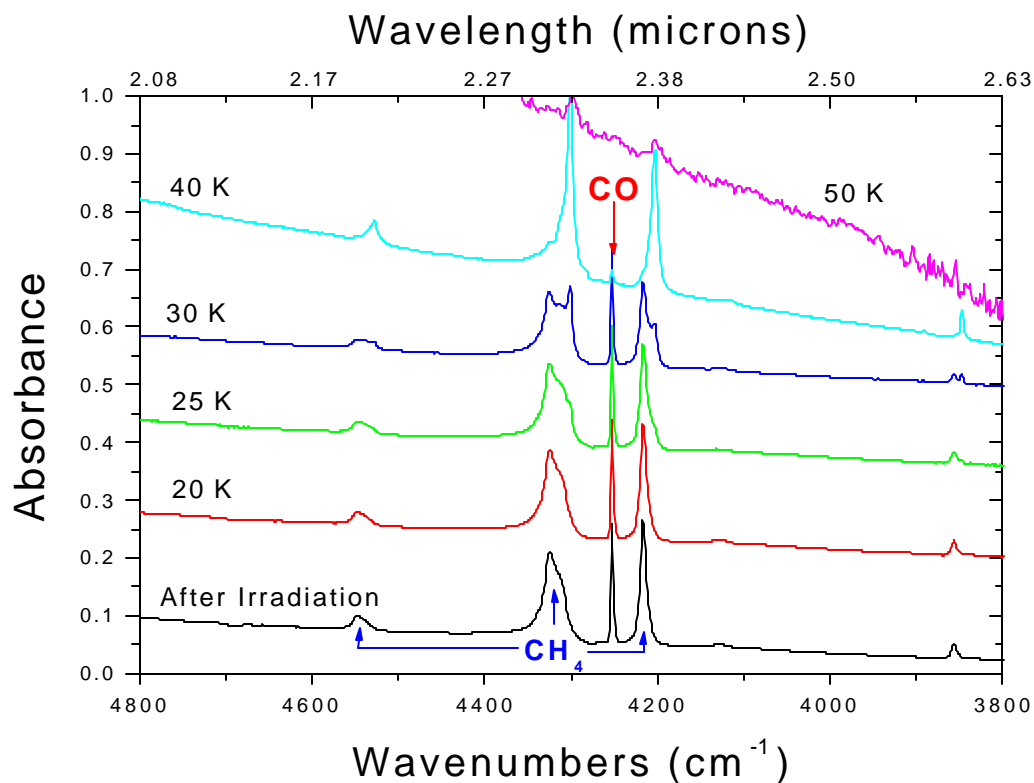
Figure 12: These spectra show the warming (annealing) of $N_2 + CH_4 + CO$ ice (20:1:1) after irradiation. As the ice is warmed, the infrared peak position is shifted toward longer wavelengths (lower frequencies, closer to the position of pure methane.

2. Identified Radiation Products of $N_2 + CH_4 + CO$ Ices

The ices most relevant to the Plutonian surface (methane and carbon monoxide doped nitrogen) were irradiated with 1 MeV protons to doses of approximately 1 eV/molecule (see appendix for calculation of dosage). Resulting radiation products were identified by comparing infrared spectra of the ices before and after irradiation and ascertaining the positions of new peaks. The new peaks were compared with known peak positions of possible radiation products or compared with reference spectra, taken in the

laboratory, of possible radiation product ices.   When peaks matched known peak positions or laboratory reference spectra, they could be assigned to a specific molecule as the radiation product.   Most radiation products were identified in the MIR region because the largest absorbance features of the chemical species being studied occur in this region, making the radiation products more readily detectable by infrared spectroscopy   (see Figure 13).

For ices consisting of a solid solution of CH_4 and CO in N_2, identified radiation products and their infrared peak positions include: C_2H_6 at 2976 cm^{-1} (3.360 ì m), 2941 cm^{-1} (3.400 ì m), and 2883 cm^{-1} (3.469 ì m); CO_2 at 2348 cm^{-1} (4.259 ì m); HCN at 3286 cm^{-1} (3.043 ì m); HCO at 1861 cm^{-1} (5.373 ì m); HNC at 3566 cm^{-1} (2.804 ì m); HNCO at 2266 cm^{-1} (4.413 ì m); and N_3 at 1657 cm^{-1} (6.035 ì m).
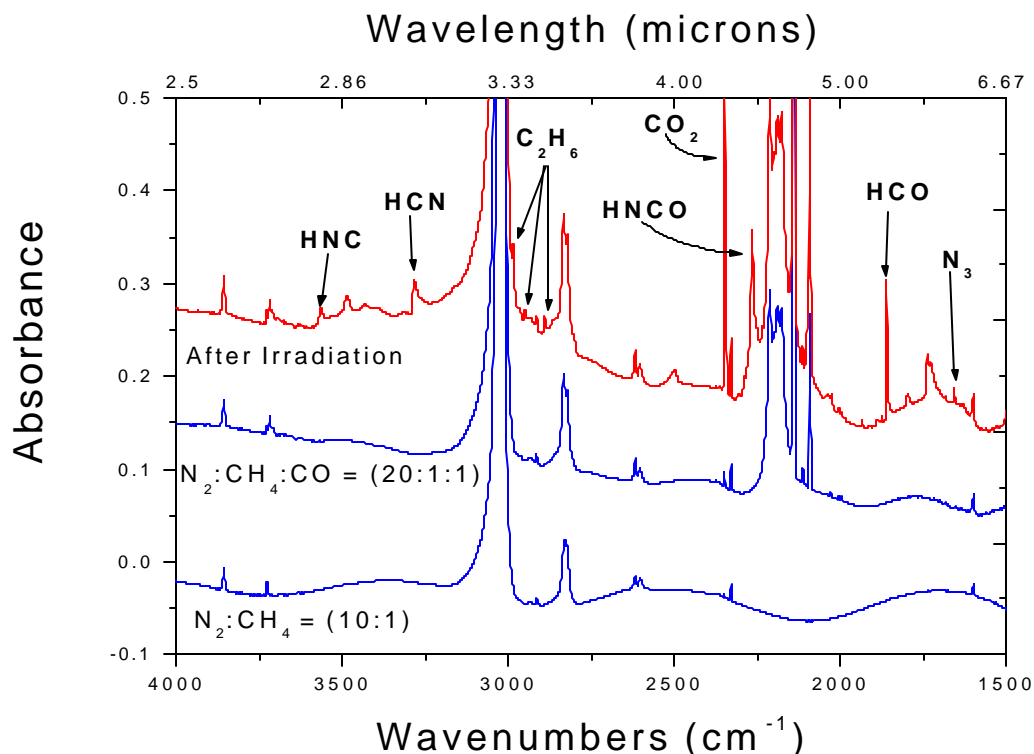
Figure 13: Identified radiation products (blue spectra indicate samples before irradiation, and the red spectrum is of the N2 + CH4 + CO ice, after irradiation)

3. Effect of CH$_4$ Concentration on C$_2$H$_6$ Production

Since recent astronomical observations of Pluto in the NIR region (by the Subaru telescope) boast the first ever identification of ethane on the planet, the possibility that ethane is a product of cosmic radiation on Pluto was extensively investigated in this project. All methane-containing ices have been found to generate some amount of ethane due to proton irradiation. However, analysis of ice spectra in which the ices contain varying concentrations of CH$_4$ in the N$_2$ matrix demonstrates that C$_2$H$_6$ production by irradiation is highly dependent on the relative concentrations of the CH$_4$ and N$_2$ in the ice. With the knowledge that total matrix isolation of CH$_4$ occurs when its concentration is

2% or less, with respect to the N_2, it is expected that little C_2H_6 production will be possible if the radiation-induced CH_4 fragments are isolated from each other and unable to combine to form C_2H_6. Presumably, this process of C_2H_6 production is carried out by the generation of methyl radicals ($CH_3\cdot$) from the irradiated CH_4 molecules in the ice, and the subsequent combination of these newly formed radicals to produce molecules of C_2H_6.

$$CH_4 \longrightarrow CH_3\cdot$$
$$\text{Proton Irradiation}$$
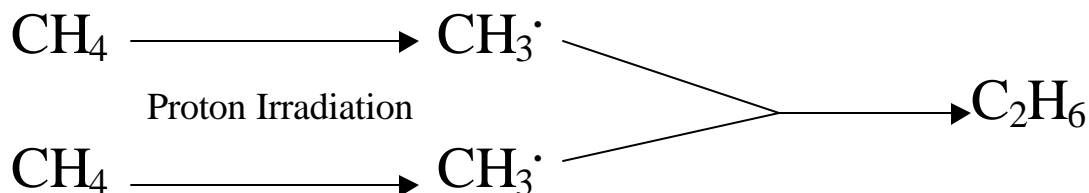$$CH_4 \longrightarrow CH_3\cdot \longrightarrow C_2H_6$$

Figure 14: Proposed mechanism by which ethane is produced from proton irradiation of methane-containing ices. Proton bombardment causes methane to break down into methyl radicals, and these methyl radicals combine, forming molecules of ethane.

As expected, laboratory experiments in which CH_4 concentration was only 1% with respect to N_2 showed very little C_2H_6 production from proton irradiation, presumably because of the lower probability for recombination of the methyl radicals in their matrix isolated state. In the irradiation of experimental ices containing CH_4 concentrations of 5% and higher with respect to the N_2 matrix, more C_2H_6 production was observed (see Figure 15), as methyl radicals could more readily move throughout the matrix to combine. Radiation experiments were performed using ices with CH_4 concentrations of 1%, 5%, 10%, 20%, and 50% relative to N_2.
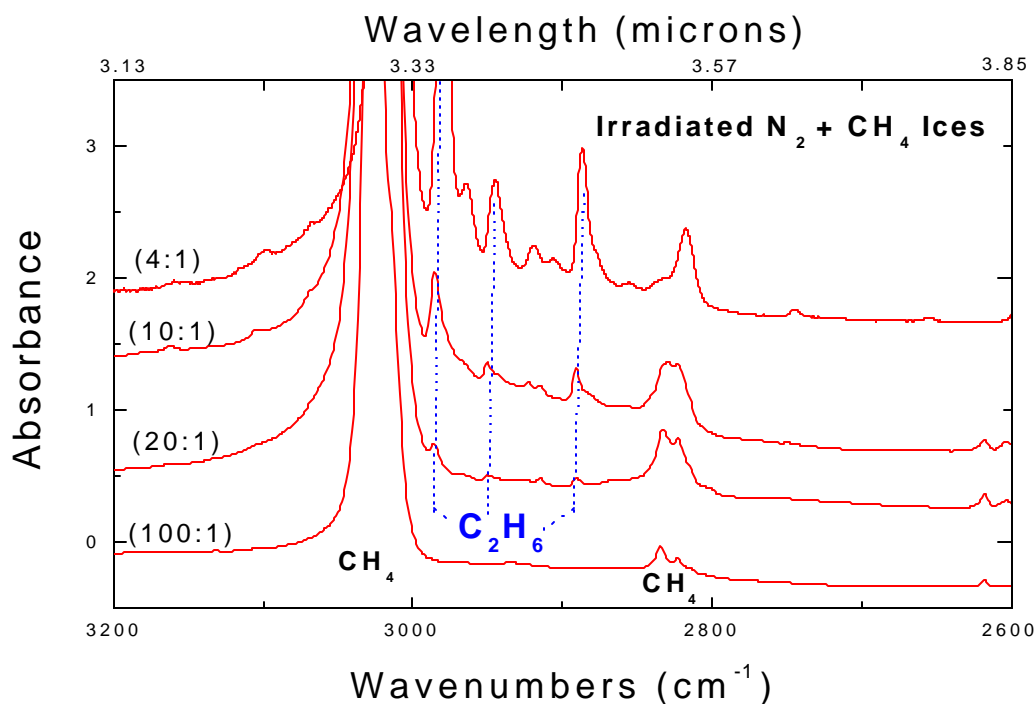
Figure 15: These spectra of proton irradiated $N_2 + CH_4$ ices show the effect of methane concentration on ethane production. The ratios shown are ($N_2 : CH_4$).

C_2H_6 production was observed in the MIR during the irradiation of ices with almost all CH_4 concentrations. However, in the same ices, C_2H_6 was not simultaneously detectable in the NIR and MIR for ices of low (<20%) CH_4 concentration (see Figure 16). This inability to detect (in the NIR) the C_2H_6, that was known to be present, occurred because the C_2H_6 absorbance features are much weaker in the NIR than in the MIR. The NIR absorbance features are weaker overtones of the molecule's primary vibrational modes, which are observed in the MIR. From these experiments, it is concluded that ices containing CH_4 concentrations of less than 20% with respect to N_2 do not allow sufficient C_2H_6 production for detection in astronomical observations taken in the NIR.
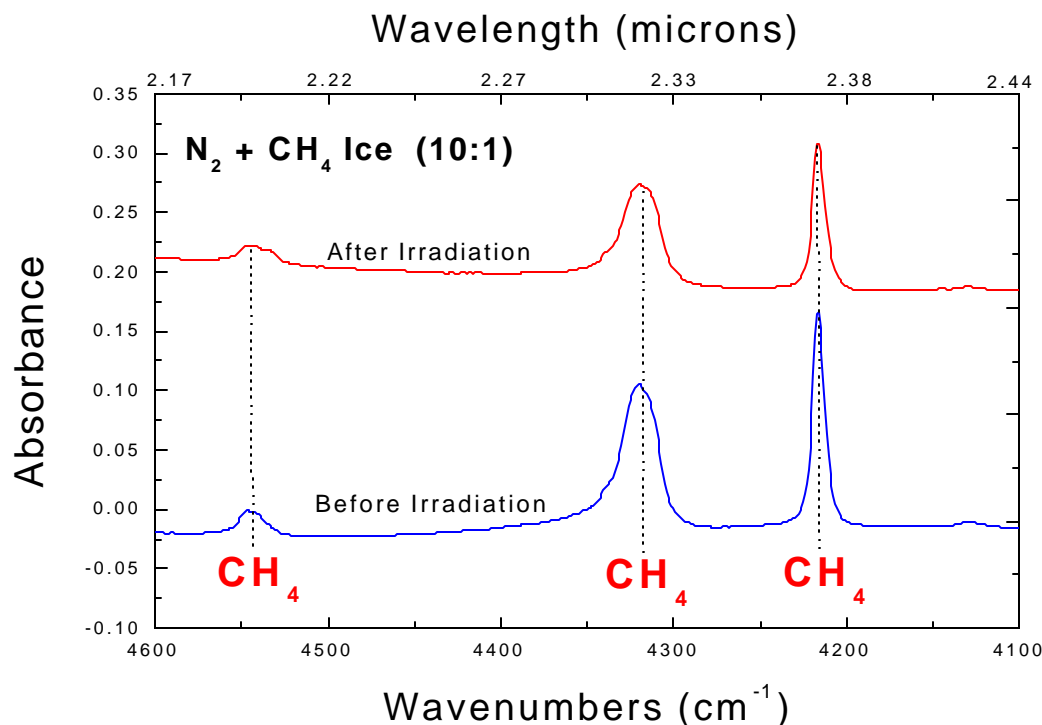
Figure 16: Specta taken before and after proton irradiation of ice containing $N_2 + CH_4$ (10:1) show no detectable C_2H_6, as a radiation product, in the NIR region. This is the same (10:1) ice sample shown in the MIR region in Figure 15, where significant C_2H_6 was detected as a radiation product.

From the perspective of planetary features, these results indicate that astronomically observable ethane produced by cosmic ray irradiation on Pluto must originate from areas of methane concentration of 20% or greater. If the surface of Pluto is really a solid solution of matrix isolated CH_4 and CO in N_2, as has been historically reported (Owen et al. 1993), then radiation-generated ethane would not be observable by ground-based infrared astronomy.   Yet since ethane has been identified in ground-based astronomical observations, as previously indicated (see Figure 6), the conclusion that Pluto's surface contains regions of high (>20%) methane concentration is justified (this

assumes that the ethane is, indeed, formed only through cosmic ray irradiation). The existence of two different terrains on the Plutonian surface, one consisting of dilute CH_4 in N_2, and the other of higher concentrations of CH_4 (perhaps including pure methane frost), has been proposed based on modeling experiments done by Doute et al. (1999). It is, however, not surprising that specific regions of high methane concentration are not detected in the infrared observation of Pluto, because such ground-based observations cannot spatially resolve any specific regions of the planet's surface. Rather, they can only describe an entire hemisphere of the planet at the time of observation. Due to this lack of spatial resolution in ground-based infrared observations, peak positions may be most descriptive of matrix isolated CH_4 and CO in the N_2 ice, when in fact, there really exist many surface regions of varying component ice concentrations being spectrally averaged by any one observation. Irradiation of regions with high methane concentration could provide observable ethane bands, superimposed on the spectra from the more common regions of low methane levels.

4. <u>C-N Bond Formation</u>

Laboratory radiation experiments have shown that proton irradiation of simple organics in nitrogen matrices induces C-N bond formation. These C-N bonds are seen in radiation products including HCN, HNC, HNCO, and OCN^- (which appears at warmer ice temperatures). Molecules containing C-N bonds are presumably formed by the radiation-induced separation of the N_2 molecule into atomic nitrogen, the radiation induced fragmentation of organic species in the ice (CH_4 and/or CO), and the subsequent combination of one or more of these organic fragments with atomic nitrogen. The

fragmentation of N_2 molecules, as a result of irradiation, has been confirmed in the laboratory by the observation of a bright green chemiluminescence of N_2-rich ices as they were being warmed after irradiation. The chemiluminescence is a result of nitrogen atoms recombining to form N_2 and emitting visible photons as a result of the energetically favored process of N—N bond formation.

Radiation experiments producing C-N bonded species have included experiments with N_2 + CH_4 ices as well as N_2 + CH_4 + CO ices. Irradiation of N_2 + CH_4 ices produces HCN, HNC, and CH_2N_2 as radiation products with C-N bonding. Radiation products of N_2 + CH_4 + CO ices include very little HCN, HNC, and CH_2N_2, but instead, HNCO is produced (as well as CO_2 and HCO) (see Figure 17). These results show that the presence of CO in the N_2 + CH_4 matrix inhibits the production of expected radiation products that do not contain oxygen. This variation in radiation products with the addition of CO to the parent ice presumably occurs because of competition between the radiation-induced fragments of CO and CH_4 for bonding to the atomic nitrogen that is present after irradiation of the ice.

Although C-N bonded species have not yet been identified in observational spectra of Pluto, it is feasible to consider the possibility that such species may exist on Pluto in trace amounts, as products of cosmic ray irradiation. The survival of these C-N bonded radiation products, on Pluto, would be dependent on their ability to weather thermal variations consisting of 30 K and 50 K temperature cycles. There is also the possibility that C-N bonded species only survive on Pluto as part of a solid crust of organic polymers. Surface regions containing such an organic crust have been proposed in recent models of Pluto's surface composition (Doute et al. 1999).
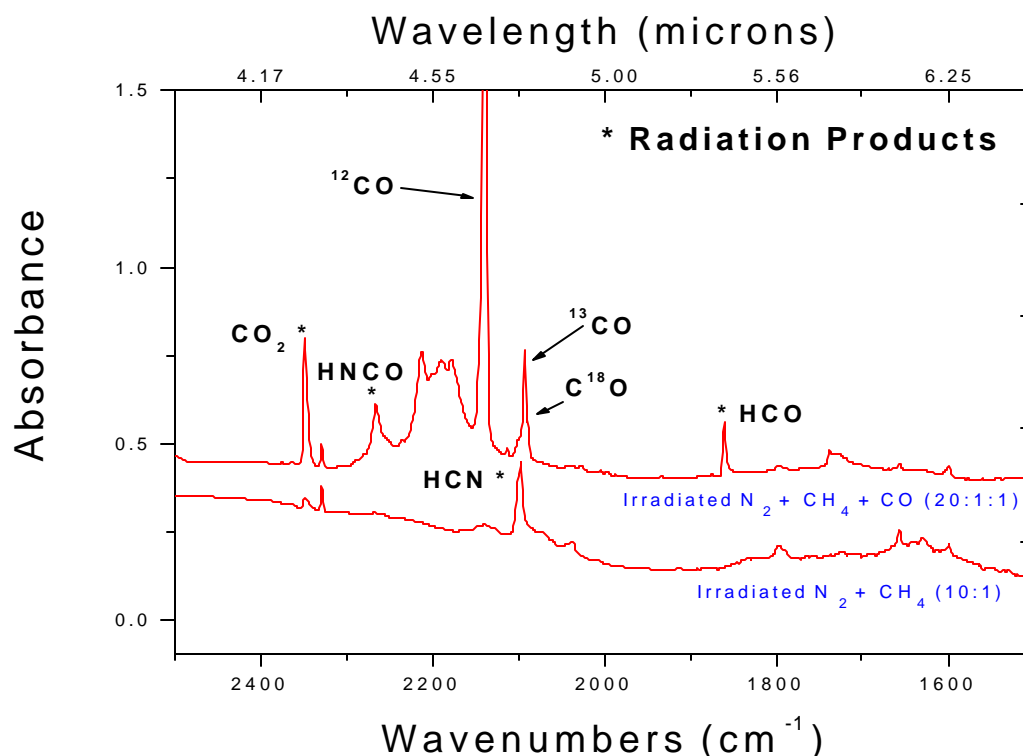
Figure 17: These spectra of irradiated ices with and without CO illustrate that the presence of CO in the
parent ice inhibits HCN production, and allows for the formation of other radiation products.

5. Laboratory Spectra vs. Astronomical Observations

        To   confirm   the   reported   identification   of   ethane   in   the   observational   Pluto

spectrum, thick ice analogs, with and without ethane, were created in the laboratory and

their infrared spectra in the NIR were compared to the Subaru telescope's astronomical

observation   (see   Figure   18).   Problems   with   this   comparison   are   noticed   due   to

differences in the relative intensity of CH_4 features between the laboratory ice spectra and

the   observational   spectrum.   Difficulties   also   arise   in   comparing   the   very   broad

reflectance   features   of   the   observational   spectrum   to   the   sharply   defined   features   of   the

laboratory spectra. The broad methane features in the observational spectrum may, in fact, be indicative of higher methane concentrations. Pure methane absorbs in wide bands in the infrared, and as methane is diluted in nitrogen ice, the bands become more narrow (like most of the laboratory spectra presented here). The broad infrared bands in the observational spectrum may be a result of spectral averaging of narrow and wide CH_4 bands at offset positions, due to various levels of CH_4 dilution in nitrogen. If so, then the broad regions of Pluto's observational spectrum may support the model describing a surface composition with regions of dilute methane and carbon monoxide in nitrogen ice and regions of high methane concentration, or even pure methane.

Using spectroscopic observations of Pluto to identify larger hydrocarbons on the surface is also made difficult by the broad CH_4 features in the spectrum. Most simple hydrocarbons absorb infrared radiation at approximately the same wavelengths because the radiation is absorbed by the vibration and stretching of the C-H bonds common to all hydrocarbons. With such broad CH_4 bands in the spectrum of Pluto, identification of other hydrocarbons, like ethane and propane, is made difficult by the masking of the entire hydrocarbon region of the spectrum by CH_4. Having evaluated this difficulty, NASA is making plans for some higher spectral resolution measurements of Pluto, by spacecraft flyby (NASA 1999). However, by assessment of the features that ethane adds to the laboratory spectrum (see Figure 18), it is clear that the broad feature between 4500 and 4400 cm^{-1} (2.22 and 2.27 ìm), in the observational spectrum, is quite suggestive of the presence of ethane.
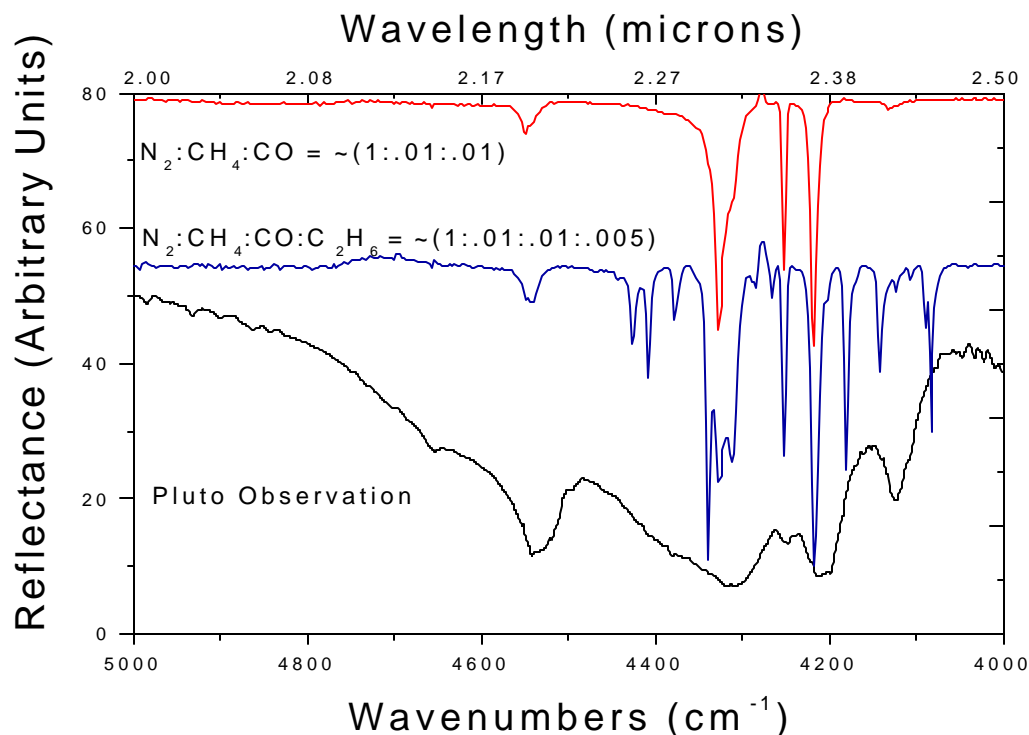
Figure 18: Comparison of laboratory ice analog spectra to an observational spectrum of Pluto

6. Viability of the Cosmic Ray Irradiation Mechanism

Cosmic ray irradiation has been shown to be the dominant energy source for inducing alterations in the icy surface of Pluto (Johnson 1989). This project investigated the correlation between the radiation environment at Pluto and the chemical conversions observed and expected on its surface. Johnson (1989) demonstrated that the Plutonian surface receives a radiation dose of 2.6×10^{18} eV/cm^2 every orbit (the orbital period is ~248 years), due to cosmic ray protons. Based on a simple model of the density of Pluto's surface ice, this radiation dosage indicates that energies of ~9×10^{-6} eV/molecule are introduced to the molecular species on Pluto, each orbit, or every 248 years (Johnson 1989). This means that over the age of the solar system (1.9×10^7 orbits, or 4.7×10^9

years), Pluto has received approximately160 eV/molecule of energy from cosmic ray protons.

In the laboratory, it was found that most radiation experiments, on ices that simulated the Plutonian surface, deposited ~1 eV/molecule of energy during a single experiment. This radiation dose was determined using parameters including the proton fluence from the Van de Graaff accelerator, kinetic energy of the incident protons, surface area of the sample, molecular density of the ice, and stopping power of the ice (see Appendix). The calculated radiation dose of ~1 eV/molecule per experiment and the information known about the radiation dosages at Pluto show that this project's laboratory experiments introduced sufficient levels of radiation to the sample ices to be relevant to the time averaged radiation environment at Pluto. The laboratory dose of 1 eV/molecule is equivalent to about 111,000 orbits (27.5 million years) worth of radiation on the Plutonian surface. The relevance to Pluto, of the radiation levels introduced to laboratory ices, indicates that the chemical conversions observed in the laboratory should, indeed, be expected on the Plutonian surface, as a result of long time constant radiation processing. The cosmic ray irradiation mechanism for the production of larger hydrocarbons and C-N bond containing molecules is certainly applicable to the surface of Pluto.

B. Analysis of Plutonian Organic Crust Analogs

When performing radiation experiments on ices containing N_2 + CH_4 and N_2 + CH_4 + CO, it was noticed that, following irradiation and thermal processing, there remained a solid, yellow colored residue on the sample substrate. These residues were

not present on the substrate before irradiation and were not a result of vacuum system contaminants, so they were deemed derivative compounds of the radiation products in the sample ices. The residues were analyzed by infrared spectroscopy at room temperature (300 K), then removed from the sample substrate by washing with methanol, and analyzed by GC-MS.

1. Production of Organic Residues

Upon warming an irradiated ice sample to room temperature (300K), only the radiation generated residue was left. These residues remain on the sample throughout the warming process, after all the other, more volatile, ice constituents have evaporated away. The residues remain on the substrate as a thin coating of yellow solid. To remain stable up to such high temperatures, these residues are presumably formed of different organic polymers, derived from the combination of the various radiation products in the ice. The organic residue that remains on the substrate at 300 K is composed of mostly nonvolatile compounds, although some volatiles may remain trapped in the organic matrix.

The most notable feature in the infrared spectra of residues derived from N_2 + CH_4 + CO ices is located at ~2160 cm^{-1} (4.630 ìm). This feature is most commonly known as the XCN band, and it is the only feature in the infrared spectra of these organic residues that maintains its intensity up to 300K (see Figure 19). XCN is the name attributed to some carrier molecule that produces the C N stretching vibrations characterized by infrared absorbance at 2160 cm^{-1}. The molecule is usually suggested to be an unidentified nitrile (X-C N) or isonitrile (X-N C) (Bernstein et al. 1995). An

alternative identification of XCN has been suggested as the CN stretch in the ion OCN[-] (Grim & Greenberg 1987).
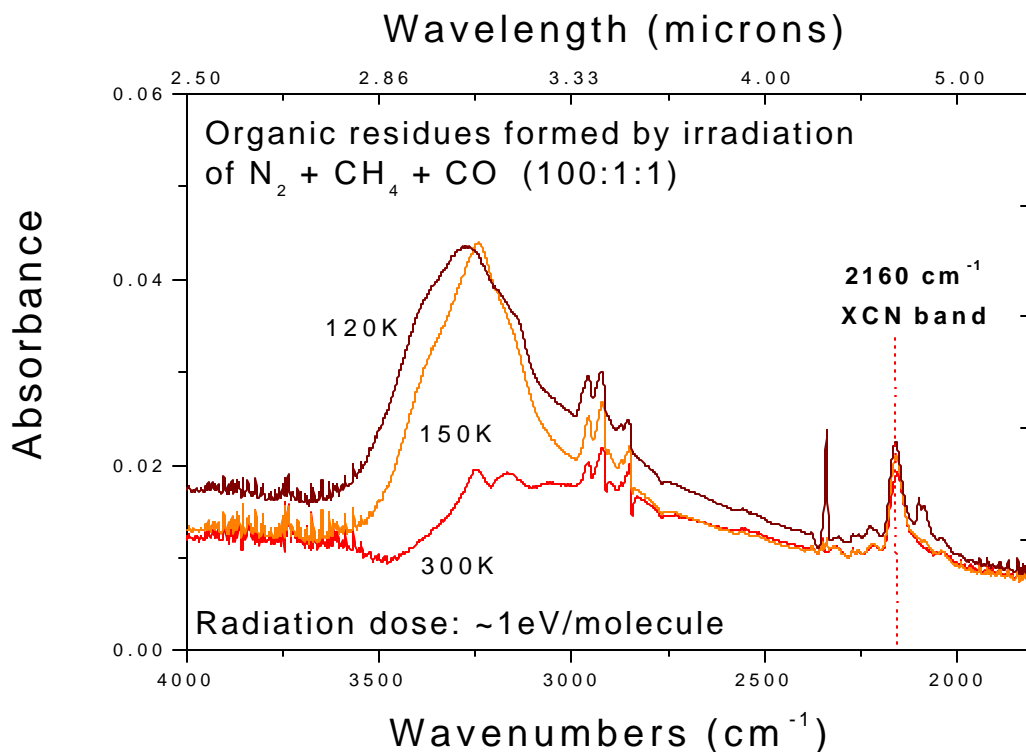

Figure 19: The warming of irradiated ices removes volatile species from the ice, leaving only the organic residue, characterized by the "XCN band" at 2160 cm^{-1}.

The identification of XCN as OCN[-] is tentatively supported by the comparison of infrared spectra of irradiated and warmed N_2 + CH_4 + CO ices and N_2 + CH_4 ices recorded during the radiation experiments of this project. Without the presence of CO in the parent ice, no source of oxygen exists to allow for OCN[-] production. In support of the identification of XCN as OCN[-], the laboratory spectra of residues derived from ices with and without CO show that the XCN feature, at 2160 cm^{-1}, is only demonstrated by the residue of the parent ice containing CO (see Figure 20). Support for the identification

of OCN⁻ in the organic residues is also demonstrated by the comparison of the residue derived from N_2 + CH_4 + CO ice with irradiated NH_4OCN. Irradiation of NH_4OCN would be expected to generate a significant amount of OCN⁻ ions by fragmentation of the molecule, so the correlation of the residue XCN feature with a collocated feature in the irradiated NH_4OCN spectrum (see Figure 20) lends more support to the presence of OCN⁻ in organic residues relevant to Pluto. Since the residue is neutral, there must be a positive ion present. However, the identity of the positive ion is not known from this analysis.
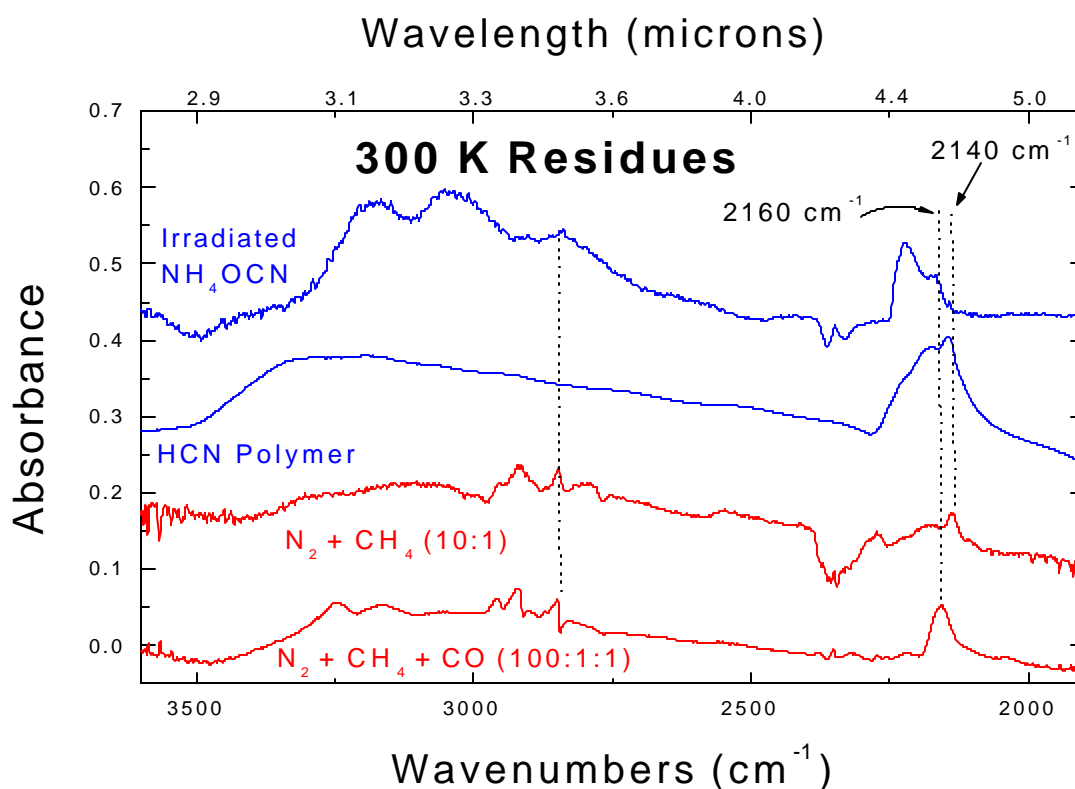

Figure 20: Comparison of organic residues relevant to Pluto and potentially similar structured species.

While residues derived from N_2 + CH_4 + CO (100:1:1) ices are relevant to the regions of Pluto's surface composed of a dilute solid solution of these constituents, they are not relevant to the regions, proposed by this project, containing higher CH_4 concentrations. Residues relevant to higher CH_4 concentration are not characterized by the XCN (or OCN^-) feature. Instead, residues derived from N_2 + CH_4 ices have a major infrared absorbance feature at ~2140 cm^{-1} (4.67 ìm). This feature lends N_2 + CH_4 derived residues to structural comparison with HCN polymers. HCN has been shown, by this project, to be a known radiation product of methane doped nitrogen ices, especially those ices which lack CO (which has been shown to inhibit HCN production). HCN polymers are formed by irradiation of HCN monomers, and can be reasonably expected to form in irradiated ices of non-matrix isolated CH_4 in N_2. As seen in Figure 20, HCN polymers do indeed demonstrate a strong absorbance feature at 2140 cm^{-1}, just as the N_2 + CH_4 derived residue does. However, the absorbance band of the HCN polymer is broader, and extends to ~2300 cm^{-1}. Organic residues relevant to regions of Pluto with higher methane concentrations may, therefore, be structurally similar to HCN polymers, whereas regions containing both CH_4 and CO may be structurally similar to the cyanate ion (OCN^-). Residues in CO containing regions may also structurally resemble HCN polymers to some degree, as evidenced by the 2160 cm^{-1} feature that is also present in the HCN polymer spectrum.

Further experimentation was performed, using GC-MS, to determine the molecular structures present in the residue derived from the N_2 + CH_4 + CO (100:1:1) ice. The gas chromatograph of the residue sample (dissolved in pure methanol) showed that there were two major constituents of the sample that were eluted from the GC

column. It is uncertain whether the constituents leaving the GC column were actually the main molecular species of the residue or simply more volatile fragments of some organic polymers that constitute the residue. However, the mass spectra of the two constituents separated by GC do offer some clues as to the possible molecular structures, or fragments thereof, that characterize the species contained in the organic residue.

The mass spectrum of the first residue constituent, identified by GC, showed its largest mass peak at 83. Since the infrared spectroscopic analysis of this particular residue suggested the presence of the OCN^- feature, it was assumed that the molecular species in the residue must contain carbon, hydrogen, oxygen, and nitrogen. Using this criterion, the major mass peaks at 83 may correlate to molecular species, in the residue, resembling C_2HN_3O, C_3HNO_2, $C_3H_3N_2O$, or C_4H_5NO (Silverstein et al. 1974). The second residue constituent, identified by GC, had its largest mass peak at 87, and using the same criterion for mass peak analysis, the peak at 87 may correlate to species resembling CHN_3O_2, CH_3N_4O, C_2HNO_3, $C_2H_3N_2O_2$, $C_2H_5N_3O$, $C_3H_5NO_2$, $C_3H_7N_2O$, or C_4H_9NO (Silverstein et al. 1974). Most of these molecular formulas correspond to unstable ions, but those corresponding to stable structures can be attributed to the molecular fragments of the organic residue injected into the GC-MS. Based on the possible structures for these stable molecular fragments, it can be deduced that the molecular species in the organic residue contain functional groups like amides, oximes, pyrrolidines, and cyanides (see Figure 21). The presence of these molecular structures may have some biochemical significance because most of the functional groups identified for possible presence in the organic residue are hydrolysis reactants for amino acid

production. This means that in the presence of liquid water, organic residues relevant to Pluto may have the potential to produce biological molecules.
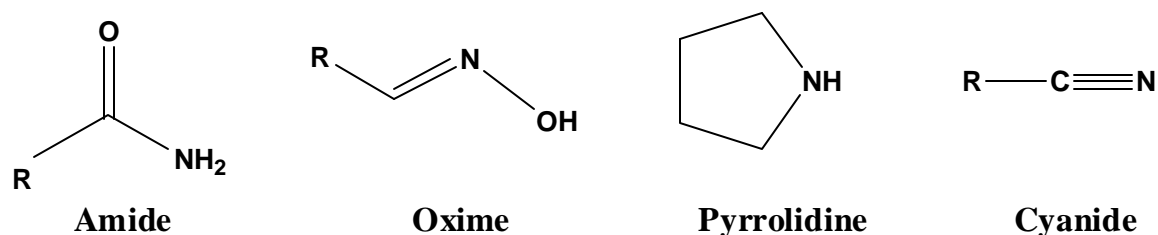

Figure 21: Structures of the chemical functional groups expected to be present in organic residues relevant to Pluto.

Although confident structural identification of the molecular species that constitute the organic residues relevant to Pluto is a difficult problem, analysis by infrared spectroscopy and GC-MS has given some valuable insight into the basic composition and structural components of the species in these residues. Such analysis has shown that there are many molecular constituents present in the residues, and certain residues contain species with OCN⁻ functionality, while others resemble HCN polymers. The relevance of these molecular species to organic crusts on Pluto is important because, at present, some unidentified, darker colored material has been detected at the equatorial regions of Pluto, and this dark material is suspected to be an organic crust which may be a product of cosmic ray bombardment of Pluto's surface ices (NASA 1999).

Furthermore, organic residues relevant to Pluto may be relevant to all objects of the Edgeworth-Kuiper Belt, including comets. Since the analysis of all the Pluto-relevant organic residues, in this project, suggests molecular structures with significant C-N

bonding, this may suggest a connection between the origin of Pluto and that of the comets of the Edgeworth-Kuiper Belt. After all, one of the earliest species identified in cometary comae was the cyanide radical (CN) (Arpigny 1965). Yet, although CN was one of the first compounds identified in comets, the source of CN remains unidentified. Perhaps the existence of a CN-rich organic crust on Pluto could finally clarify some of the long-standing questions concerning Pluto's relationship to the comets, and their implications relating to the origin of the solar system.

2. Exobiological Analysis of Organic Residues

Exobiology is the study of life's origin, evolution, and distribution in the universe. The biogenic molecules responsible for the emergence of life on Earth have been traditionally viewed as emerging from a planetary process. However, under recent scrutiny, this theory has been discredited by the knowledge that the primitive terrestrial atmosphere was, at best, only slightly oxidizing, and not reducing, as required by the theory of planetary synthesis of biogenic molecules (Chyba & Sagan 1992). In this light, a potential cometary source of prebiotic organics (the precursors of biological polymers) has found some acceptance, since a reducing atmosphere rich in CH_4 and N_2 (abundant on EKOs and other comets) could readily provide the precursors for prebiotic molecules. This exogenous source of prebiotic organics on early Earth could provide an alternative method of accounting for the terrestrial inventory of prebiotic molecules needed for the origin of life (Chyba et al. 1994).

The production of dark or reddish organic residues called "tholins" is known to occur by the energetic processing of some cosmic ices, but mainly those rich in nitrogen

and methane (Khare et al. 1984). These tholins may be the very type of material delivered to Earth by the consistent comet and asteroid bombardment that is known to have occurred during the infancy of the solar system. Experimentation has also shown that the hydrolysis of some tholins results in amino acid production (Khare et al. 1983). These studies have led to a theory that tholins, when introduced into an 'energetic' liquid water environment (like the primordial oceans and electrical/radiation activity of the early Earth), have the potential to produce biologically significant molecules (see Figure 22).
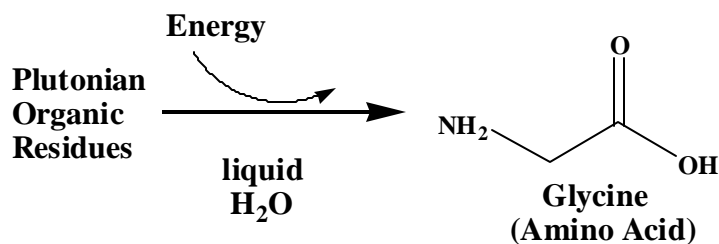

Figure 22: The chemical conversion of tholin (relevant to the outer solar system or Pluto) to biologically significant molecules like glycine, the structurally simplest of the amino acids. This conversion requires a liquid water environment and energy.

The introduction of tholins and other prebiotic molecules to the early Earth is supported by the theory of exogenous delivery of organics via interstellar dust, comet, and asteroid impacts with the infant Earth (see Figure 23). Many of these impactors are thought to have originated in the Edgeworth-Kuiper Belt, and impacted Earth during the heavy bombardment period 3.85 – 4.25 Gyrs (1 Gyr = 10^9 years) ago (Chyba & Sagan 1992). The significance of exogenous delivery to the origin of life on Earth lies in the conception that the first terrestrial amino acids and nucleotide bases (or their precursors) may have arrived on Earth during the heavy bombardment period, and in the 'energetic,'

watery environment of the primordial oceans, given rise to the first "living" microorganisms on Earth. Regarding the formation of the first organisms, NASA's astrobiology initiative has suggested that:

> "the biomolecules of life became enclosed within a lipid membrane, forming rudimentary assemblages that resembled cells as we know them, or protocells. Among the essential protocellular functions were the acquisition and transduction of energy from the environment, and catalysis to support the synthesis of cellular components (metabolism) and information transfer to succeeding generations (genetics)." (NASA/Ames Research Center)

These first organisms, in the struggle for life, are thought to have existed as "ribo-organisms," containing their genetic code on molecules of ribonucleic acids or RNA (Ridley 1999). Eventually, the more robust deoxyribonucleic acid (DNA) was invented by these organisms, allowing for efficient reproduction and evolution. Finally, Luca (the last universal common ancestor) was born, and she is thought to have been a bacterium-like "proto-ribosome" living in a warm primordial pond, gaining her livelihood from molecular species like amino acids and nucleotides (Ridley 1999).

Figure 23:
This illustration is an artist's conception of exogenous delivery of organics, and possibly prebiotic molecules, to Earth, from the outer solar system.

(Illustration by Roger Arno, NASA)

The analysis of organic residues, derived from proton irradiation of ices relevant to Pluto (and most EKOs) supports the theory that exogenous delivery of biomolecules or prebiotic molecules to the early Earth, from the Edgeworth-Kuiper Belt, may have played a role in the advent of life on Earth. The organic residues derived from ices relevant to the two main compositional regions of Pluto, examined by this project, were compared to some significant biomolecules and proven prebiotic material relevant to the outer solar system. Infrared specta of residues derived from matrix isolated ices of N_2 + CH_4 + CO and ices of N_2 + CH_4 with higher CH_4 concentration were compared to the spectra of biomolecules, glycine and urea (see Figure 24). Glycine is the structurally simplest of the amino acids, and urea is a diamide and a waste product from the metabolism of protein. The spectra of the Plutonian relevant residues were also compared to the spectrum of Titan tholin, produced at the Laboratory for Planetary Studies at Cornell University, as a part of the research of B.N. Khare and Carl Sagan. This tholin was produced by electric

discharge through a gas mixture of N_2 + CH_4, thought to be relevant to the organic haze detected on Titan (a moon of Saturn) by Voyager I (Khare et al. 1984). The tholin samples were analyzed in the laboratory at NASA/Goddard Space Flight Center by infrared spectroscopy, and have been shown, upon processing with liquid water, to reveal over 75 separate compounds, including many molecules of fundamental biological significance on Earth (Khare et al. 1984). Therefore, Titan tholin is considered a prebiotic substance relevant to the outer solar system, and pertinent for comparison with organic residues relevant to Pluto and the Edgeworth-Kuiper Belt.
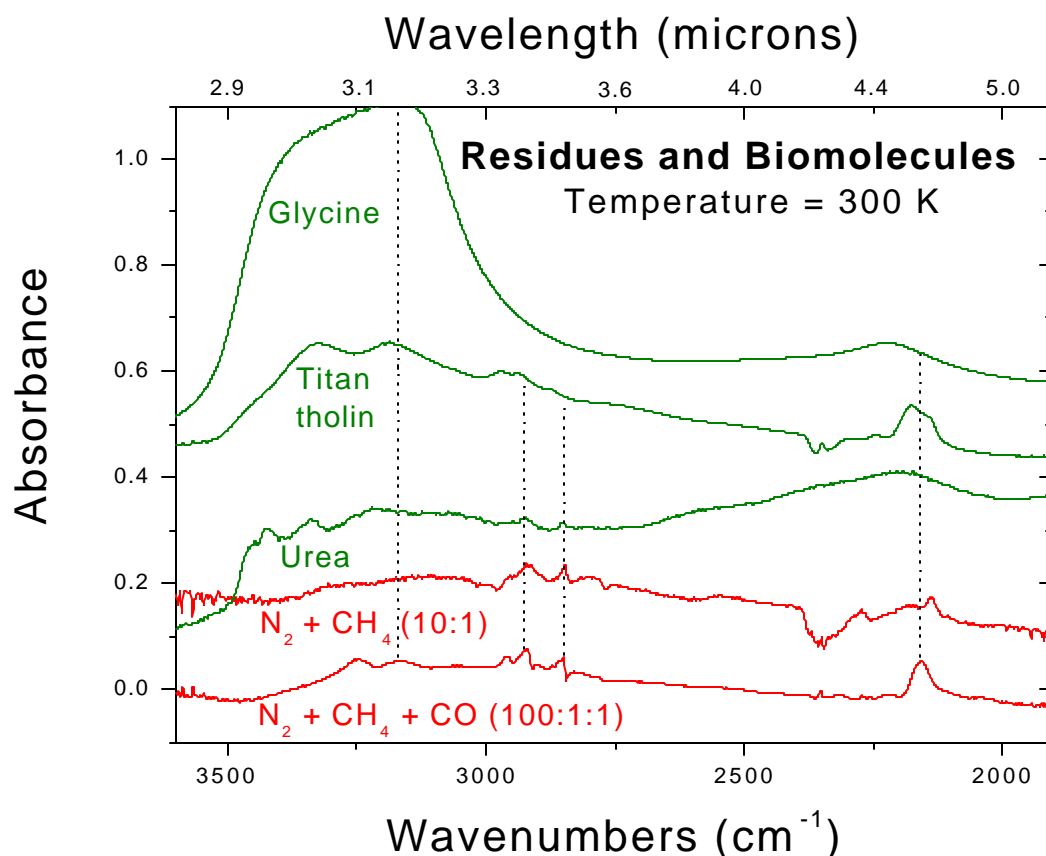

Figure 24: Comparison of organic residues relevant to Pluto and biological/prebiotic molecules.

The comparison of the infrared spectra of Plutonian relevant residues, the biomolecules, and tholin shows collocated peaks at 2848 cm^{-1} (3.51 ìm) and 2924 cm^{-1} (3.42 ìm) for both organic residues, urea, and tholin (see Figure 24). These features are attributable to the C-H stretching, common to hydrocarbon chains. The XCN (or OCN^{-}) feature at 2160 cm^{-1} (4.63 ìm) in the spectrum of the N$_2$ + CH$_4$ + CO derived residue is also common to urea, tholin, and glycine, though the band is sometimes broadened between 2170 cm^{-1} and 2160 cm^{-1}. The spectrum of the N$_2$ + CH$_4$ + CO derived residue also shares a peak with glycine and tholin at 3163 cm^{-1} (3.16 ìm), probably attributable to C-H stretching. Although, the spectrum of the residue derived from N$_2$ + CH$_4$ ice does not match the biomolecule spectra at its 2140 cm^{-1} feature, it does match the same feature in the HCN polymer spectrum. This correlation may have biochemical significance as HCN polymers have been found to have structural subunits of many types: diacyl, amino acyl, purine/pyrimidine, and triazine (Minard et al. 1998). These functional groups are similar, but more complex, versions of the structures pictured in Figure 21, and they too are relevant to biochemistry.

The multiple structural similarities, suggested by infrared spectra, between organic residues relevant to Pluto and biologically relevant molecules are very significant. The structural similarities of these molecules imply the possibility that compounds related to the origin of life on Earth may have had their beginnings on the icy bodies of the outer solar system, and may have been delivered exogenously to the early Earth. It is important to further investigate this possibility and make every effort to understand the chemical and physical origins of the biosphere in which we now dwell.

V. <u>Conclusions</u>

Based on the viability of the cosmic ray irradiation mechanism for chemical conversions in cosmic ice analogs, and the observed radiation products in laboratory radiation experiments involving ices relevant to Pluto, it is concluded that the Plutonian surface is comprised of various regions with multiple compositions. In general, the degree of CH_4 concentration in the various regions affects the radiation products generated by cosmic ray irradiation and the composition of the organic residues expected to be present there. All surface ices on Pluto are expected to generate radiation products of CO_2, N_3, and HCN (in varying amounts), and all organic residues are expected to consist of various organic polymers.

Some of the Plutonian surface is a solid solution of N_2 + CH_4 + CO in which the CH_4 and CO are matrix isolated in the nitrogen ice. In these regions, relative CH_4 and CO concentrations, with respect to N_2 ice, are 1% and less. Products of cosmic ray irradiation, containing C-N bonds, expected here in trace amounts, are HCN and HNCO, and another unique radiation product is HCO. These regions of matrix isolated CH_4 and CO in N_2 ice produce insubstantial amounts of larger hydrocarbons as a result of cosmic ray irradiation, but they do generate organic residues characterized by the OCN^- feature and possibly of some exobiological significance. These organic residues may be similar in structure to biomolecules like glycine and urea, and may also resemble proven prebiotic material like tholin. Since Pluto is thought to have links to other EKOs, like comets, such exobiologically significant organic residues could account for the exogenous delivery of prebiotic organics to the early Earth via comet bombardment.

Other regions of Pluto's surface contain high (>20%) CH_4 concentrations, relative to N_2 ice, and produce substantial amounts of C_2H_6 (and possibly larger hydrocarbons) as a result of cosmic ray irradiation of the CH_4 in the ice. It is the C_2H_6 generated here that is detectable by ground-based NIR observations. Radiation products containing C-N bonds, such as HCN and HNC are produced in greater amounts in these regions. Cosmic ray irradiation and thermal processing in these regions also generates some organic residues. The organic residues generated here may structurally resemble HCN polymers, possibly having subunits relevant to biochemically active compounds.

Analysis of the radiation chemistry on the Plutonian surface has unveiled a diverse and complex model for the surface composition on the planet. The conclusions of this project represent a more comprehensive description of the various surface regions on Pluto, and the dynamic radiation processes occurring there, than has been previously produced by laboratory research.

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Appendix

Methods for Laboratory Radiation Dosage Calculations

The radiation dose (in eV/molecule) experienced by a given ice sample, irradiated with
1 MeV protons, is calculated as:

This relation reduces to:

In this equation, proton fluence is dependent on the number of "counts" of radiation
received from the Van de Graaff accelerator by the sample. These counts are a measure
of the integrated proton beam current at the sample, and relate to incident proton fluence
as follows:

Current Scale (A)	Fluence per count (P^+/cm^2)	*sample area is
3×10^{-7}	3.694×10^{11}	1" diameter circle,
10×10^{-8}	1.23×10^{11}	$A = 5.067$ cm^2
3×10^{-8}	6.394×10^{10}	

S is the stopping power, in MeV cm^2 g^{-1}, of the ice, or the ability of the ice to absorb the
kinetic energy of the incident protons. Since the stopping power of water ice is known, it
is convenient to solve the ratio of the stopping power of nitrogen ice to stopping power of
water ice.

where: m_o is the mass of an electron
   v is the velocity of the incident radiation
   I is the mean excitation energy of each compound

The mean excitation energy for a molecule can be computed using Bragg's rule:

$$I^N = I_1^{N_1} \times I_2^{N_2} \times I_3^{N_3} \times ...$$

where: N = total number of electrons in the molecule
   N_i = number of electrons for atom type 'i'   (Note: $N = \Sigma N_i$)
   I = mean excitation energy of the molecule

I_i = mean excitation energy of atom type 'i' in the molecule

Note: $I_{nitrogen} = 90eV$

$$t = \frac{1}{2(\Delta \boldsymbol{n})} * \frac{10^4}{n}$$

$$\frac{eV}{molecule} = \frac{(incident\ fluence)\ x\ S\ x\ 10^6 eV/MeV}{(formula\ weight)^{-1}\ x\ 6.022\ x\ 10^{23}}$$

$$\frac{eV}{molecule} = \frac{(incident\ fluence)\ x\ S\ x\ thickness\ x\ density\ x\ area\ x\ 10^6\ eV/MeV}{thickness\ x\ density\ x\ area\ x\ (formula\ weight)^{-1}\ x\ 6.022\ x\ 10^{23}}$$

$$S\ (N_2) = S\ (H_2O)\ x\ \frac{\#\ e^-\ per\ N_2}{\#\ e^-\ per\ H_2O}\ x\ \frac{N_2\ density}{H_2O\ density}\ x\ \frac{H_2O\ molecular\ weight}{N_2\ molecular\ weight}\ x\ \frac{\ln\left(\frac{2m_o v^2}{I_{N_2}}\right)}{\ln\left(\frac{2m_o v^2}{I_{H_2O}}\right)}$$